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Resonant enhancement of inverse photoemission transitions in bulk niobium

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We report the observation of the resonant enhancement of inverse photoemission transitions involving bulk band states of niobium when the energy of the transition corresponds to the plasma frequency. On resonance the cross section increases by a factor of ~5. Comparison with earlier reflectivity data confirms that the resonance occurs at the plasma frequency but the measured plasmon energy of 19.3 eV is slightly less than the 20.8 eV found in the earlier study. We do not observe resonant enhancement of transitions into surface states or interface states.

It has recently been reported that inverse photoemission transitions show a strong enhancement or resonant behavior when the energy of the transition corresponds to the plasma frequency of the material.[1,2] Drube and Himpsel[1] first reported the observation for antimony thin films grown on different substrates. These authors also reported that experiments on aluminum, tungsten, and a few other materials, did not show the same phenomenon. In a subsequent paper Drube, Himpsel, and Feibelman[3] reported the observation of the inverse surface photoeffect from aluminum surfaces, i.e., rather than an intensity maximum at the plasma frequency an intensity minimum was observed. The intensity minimum in the surface photoeffect is generally interpreted in terms of continuity of the fields across the solid-vacuum interface. At the plasma frequency the photon field excites bulk plasmons which serve to screen the A_z component inside the metal. The inverse surface photoeffect was seen as directly related to this same mechanism through "time reversal."

In free-electron materials, bulk plasmons, longitudinal excitations, will couple to transverse photons only at the surface; surface plasmons will decay into photons only if momentum is conserved through the intervention of surface roughness. The coupling between photons and plasmons in thin films has, however, been the subject of a number of investigations both theoretical and experimental. Ferrell[4] predicted that plasmons, excited by energetic electrons entering the thin film, would be able to decay into photons resulting in the emission of light at the bulk plasma frequency w_p. Kliewer and Fuchs[5] found that there exists a large number of virtual plasmon modes in thin films. Of these, however, they found only one mode which had an electric field that was not decaying exponentially outside of the film. This radiative mode is the source of the optical plasma resonance phenomena, reviewed extensively by Steinmann.[6] It has been observed that there is an enhanced photoyield from thin films when the photon energy corresponds to the plasma frequency.[7] This latter observation has been interpreted in terms of an enhanced transmittivity of the photon field into the film at the plasma frequency. These observations raise the question as to whether the enhanced inverse photoemission cross sections at the plasma frequency were an artifact of the thin film[1] or layered material,[2] particularly in view of the lack of observation of the same phenomena in a number of other materials. In this paper we present results showing the resonant behavior occurring for well-defined bulk transitions, a demonstration that it is not restricted to thin films. The present studies were conducted on two niobium single crystals: one with the ⟨110⟩ direction oriented along the surface normal and the second with the ⟨100⟩ direction along the normal. Spectra from these two surfaces clearly show both the decay of plasmons into photons and also the resonant enhancement of the bulk transitions at the plasma frequency.

The single-crystal niobium (110) surface was produced by recrystallizing a niobium foil through repeated annealing to 2000 °C.[8] The second surface was a single crystal oriented by Laue diffraction and cut to expose the (100) surface. Surface order and cleanliness were monitored with low-energy electron diffraction and Auger electron spectroscopy, respectively. Inverse photoemission spectra were recorded using an instrument that has been described in detail elsewhere.[9] Briefly, a normal incidence spectrograph is used to collect photons in an energy range from 10–35 eV. The electron-beam is provided by a low-energy electron source designed for inverse photoemission studies. The overall energy resolution of the system varies from 0.3 eV at the low energies to 1 eV at the higher energies ($>$ 30 eV).

In Fig. 1 we show inverse photoemission spectra recorded for the electron beam incident along the surface normal of the (110) crystal. The different electron beam energies with respect to the Fermi level are indicated. We identify two characteristic features in these spectra. The first, a strong feature at the fixed final-state energy 3.5 eV above the Fermi level, that we have previously identified as due to direct transitions into unoccupied d bands of Σ_4 and Σ_1 character.[10] The second feature, identified by the dashed line, occurs at a fixed photon energy even though the incident electron-beam energy is varied. This constant photon energy of 19.3 eV is close to the energy of a strong resonance previously observed in the volume loss spectrum in reflectivity studies from niobium.[11] It was suggested that the loss peak reflected the production of bulk plasmon resonances. We therefore associate the peak at constant photon energy in our spectrum with the decay of bulk plasmons either directly or indirectly into photons. A plasmon frequency of 19.3 eV for niobium is lower than the value of 20.8 eV derived from the reflectivity data. It

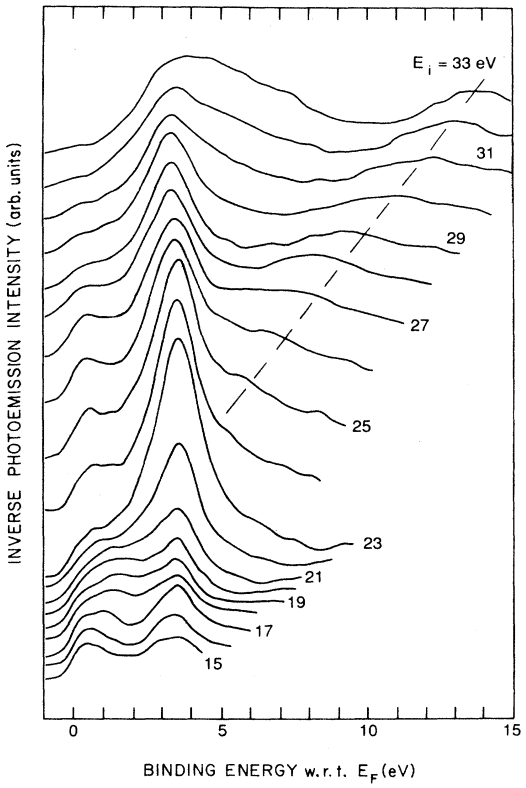

FIG. 1. Inverse photoemission spectra recorded from a Nb(110) surface as a function of the incident electron-beam energy. The dashed line indicates the position of the plasmon peak at fixed photon energy. (w.r.t. denotes with respect to.)

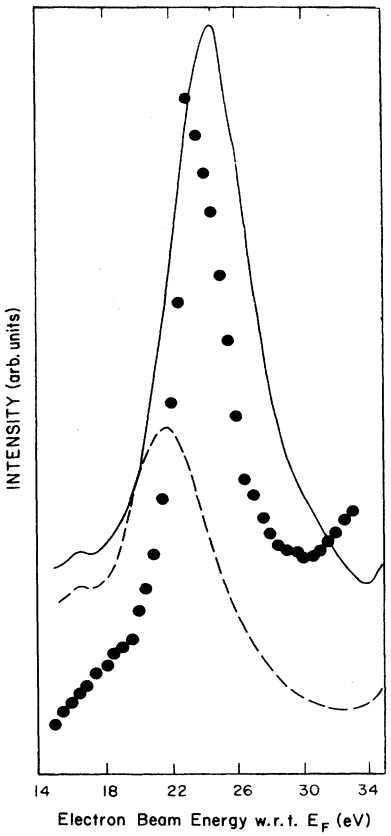

FIG. 2. Intensity of the direct transition 3.5 eV above the Fermi level in Fig. 1 as a function of the incident electron-beam energy. The solid line represents the bulk loss function for niobium derived from reflectivity data (Ref. 11) and the dashed line represents the surface loss function.

is, however, closer to the value of 19.7 eV found in earlier electron loss studies[12] and also surprisingly close to 19.56 eV, the plasma energy of a free-electron gas with the parameters of Nb.

Figure 1 shows that when the plasmon peak coincides with the direct transition there is a strong enhancement of the intensity of that transition. As noted in the earlier study[1] the enhancement is greater than the sum of the two individual components. In Fig. 2 we plot the intensity of the unoccupied *d* band, 3.5 eV above the Fermi level, as a function of the incident electron-beam energy. A measure of the intensity is obtained simply by measuring the height of the peak above a linear background. We also show in Fig. 2 the loss function $\mathrm{Im}(1/|\varepsilon|)$ and the surface loss function $\mathrm{Im}(1/|\varepsilon+1|)$, both displaced by 3.5 eV, from the reflectivity data of Weaver, Lynch, and Olsen.[11] It will be seen that there is again reasonable agreement between the peak in the *d*-band intensity and the peak in the bulk loss function, the former being at approximately 23.0 eV and the latter at 24.3 eV. The possibility that the intensity maximum arises from a density-of-states effect relating to some initial state we believe is ruled out because we note that at the same initial-state energy there is no rise in the intensity of a band immediately above the Fermi level.[10]

We have reported our observations following the deposition of palladium on the Nb(110) substrate elsewhere.[13] Here, we note that the plasmon enhanced resonance observed for the clean surface is completely preserved on the same surface covered with two monolayers of palladium. Indeed there is no change in either the resonance or the photon intensity derived directly from the plasmon decay. The persistence of the resonance in the presence of the overlayer serves to confirm the observation that the resonant transition involves bulk states. The deposition of palladium on the niobium (110) substrate leads to the formation of a two-dimensional interface state.[12] This state is predominantly niobium derived and because of its localization shows no dispersion with $k_\perp$. It does not show any resonant behavior.

In Fig. 3 we show inverse photoemission spectra recorded from the Nb(001) surface as a function of the incident electron-beam energy. We identify three features in these spectra: a peak at the constant photon energy of 19.3 eV and peaks at constant final-state energies of approximately 3.5 and 0.3 eV, respectively. The peak at constant photon energy, identified by the dashed line, again results from the decay of plasmons into photons. The other two peaks represent direct radiative transitions, one into the bulk Δ_1 band, 3.5 eV above the Fermi level, and the other into a surface state in the vicinity of the Fermi level. The

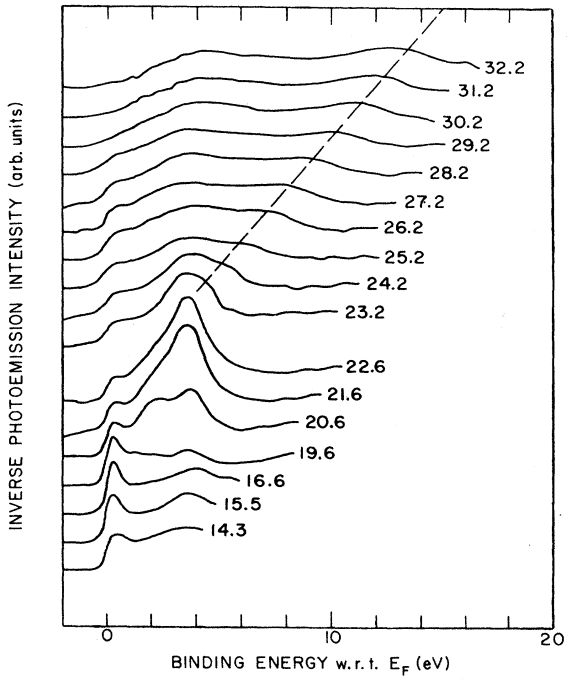

FIG. 3. Inverse photoemission spectra recorded from a Nb(100) surface as a function of the incident electron-beam energy. The dashed line indicates the position of the plasmon peak at fixed photon energy.

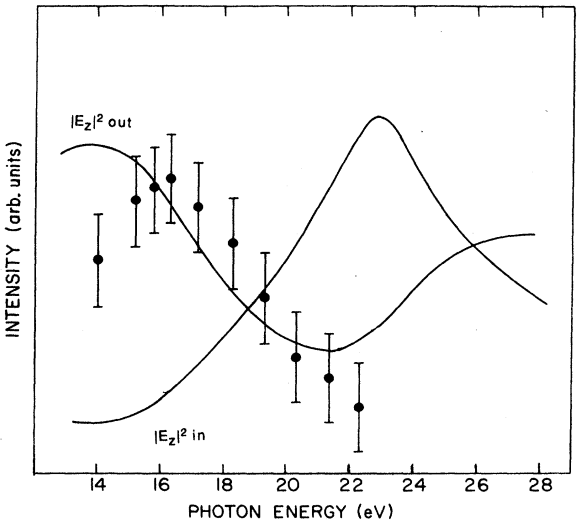

FIG. 4. Intensity of the surface state immediately above the Fermi level in Fig. 3 as a function of photon energy. The experimental points are compared with the calculated Fresnel fields inside and outside of the surface.

observation of this d_{z^2}-type surface state, theoretically predicted to lie 0.2 eV above E_F at $\bar{\Gamma}$,[14,15] was recently reported in a photoemission study.[16]

In Fig. 4 we follow the earlier photoemission study and compare the measured cross section of the surface state in Fig. 3 with the macroscopic Fresnel or electric fields present at the solid-vacuum interface as determined from the measured optical properties of niobium. We note that the photon energy dependence of the bulk Δ_1 band on this Nb(001) surface is identical to that of the Σ_4/Σ_1 complex on the Nb(110) surface, i.e., a strong enhancement at the plasmon frequency. It will be seen in Fig. 4 that the surface state does not resonate at the bulk plasmon energy. Indeed its photon energy dependence in the present experiment is similar to that observed in the photoemission study, where it was found that the intensity closely followed the wavelength dependence of the external electric field. This was taken as an indication of the localization of the state in the surface region as found in the calculations. As we do not appear to detect surface plasmons decaying into photons in the present study we are unable to say whether the intensity maximum reflects the alternative possibility of a resonance at the surface-plasmon frequency. However, we note that the broad maximum in the surface-state cross section is considerably less well defined than the sharp plasmon resonance for the bulk states.

Our experimental observations clearly show that the resonant enhancement of the inverse photoemission transitions is not necessarily restricted to thin films but is, in fact, observable for well-defined bulk transitions. We have not, however, observed the same behavior for either surface states or interface states. The resonant enhancement represents an interaction between a discrete channel (plasmon production) and a continuum (the inverse photoemission transition). Wendin and Nuroh[17] have discussed the possibility of resonant inverse photoemission involving coupling between such channels. He finds that on resonance the intensity of the peak reflects both the excitation probability for the discrete intermediate level and also the alternative decay mechanisms available to this channel plasmon. It was reported that resonant enhancement was not observed in the free-electron-like material aluminum elsewhere.[3] This presumably reflects the coupling between the longitudinal excitation the plasmon and the transverse field of the photon. In a free-electron metal such a coupling is not allowed. However, in a periodic lattice the stronger scattering potential will be available to mediate the coupling. Thus the process may be viewed as the excitation of an intermediate discrete channel, an electron-hole pair, or an effective plasmon. Sturm and Oliviera[18] have considered the role of local-field effects in photon-plasmon coupling. Their study suggests that in aluminum with a weak scattering potential the coupling would be small or nonexistent. Conversely, in the transition metals such as those studied here, one anticipates that the coupling will reflect the stronger scattering potentials.

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